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Oxy Silanes

METHOD FOR MANUFACTURING A LIGHT-TRANSMITTING  
QUARTZ GLASS BASE MATERIAL

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1. Title of the Invention: METHOD FOR MANUFACTURING A  
LIGHT-TRANSMITTING QUARTZ  
GLASS BASE MATERIAL

2. Claim

A method for manufacturing a light-transmitting quartz glass base material wherein an estersilane represented by the following general formula:  $R_1^nSi(OR^2)_{4-n}$  (wherein  $R^1$  is selected from among a hydrogen atom, methyl group, and an ethyl group;  $R^2$  is selected from between a methyl group and an ethyl group;  $n$  is a positive number of 0-4) and a dopant represented by one of the following formulae:  $Ge(OR^3)_4$  or  $B(OR^3)_3$  (wherein  $R^3$  is a monovalent hydrocarbon group) or  $PH_3$  are heated and combusted in a quartz tube in such a way that the resulting dopant-containing silica will be deposited on the inner wall of said quartz tube as a transparent glass film and wherein said quartz glass tube is heated and melted for the purpose of eliminating the hollow segment of said quartz tube.

3. Detailed explanation of the invention

The present invention concerns a method for manufacturing a light-transmitting quartz glass base material. More specifically, the present invention concerns a method for manufacturing a light-transmitting quartz glass base material which contains no chlorine (as element or compound) by the internal MCVDA method.

There are various conventionally-known techniques for

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\*Numbers in margin indicate pagination in foreign text.

manufacturing light-transmitting quartz glass base materials. In any event, the purity of said material must be extremely high, and the refractive index in the cross-sectional direction must be carefully controlled. For these reasons, the chemical vapor-phase deposition method (CVD method), wherein a chemical reaction is utilized, is commonly utilized. Said CVD method can be further classified into the internal method (MCVD) method, wherein a silica which has been obtained by oxidizing a silicon-containing compound is formed as a transparent glass film on the inner wall of a quartz tube, the external method, wherein a silica which has been prepared by flame-hydrolyzing a silicon-containing compound is deposited on the outer surface of a core material, and the vapor-phase /2 axial deposition method (VAD method), wherein a silica which has been obtained by flame-hydrolyzing a silicon-containing compound is deposited on a rotating refractory material in a cylindrical fashion. Said external method and VAD method are different from the MCVD method in that reactions are not induced in closed systems. For this reason, it is difficult to control the refractive index of the glass base material. When a high-quality optical fiber is manufactured, therefore, the internal MCVD method, wherein the dopant concentration can be easily controlled, is preferred.

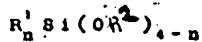
When a typical conventional internal MCVD method is implemented, a mixture consisting of a glass-forming gas (i.e., silicon tetrachloride ( $SiCl_4$ )), a dopant for controlling the glass refractive index (e.g., germanium tetrachloride ( $GeCl_4$ ), phosphorus

oxychloride ( $\text{POCl}_3$ ), boron trichloride ( $\text{BCl}_3$ ), etc.), and gaseous oxygen (i.e., oxidizing gas) is fed into one end of a quartz tube, and said gaseous mixture is heated by transporting an oxyoxygen flame burner or an electrical resistant heater between the inlet and outlet sides of the exterior of said quartz tube. A dopant-containing silica which has been produced as a result of vapor-phase oxidation is deposited in the longitudinal direction of the inner wall of the quartz tube as a transparent glass film. Subsequently, the hollow segment of said quartz tube equipped with said glass film layer is eliminated in order to manufacture a quartz glass base material. The quartz glass base material which has been obtained in this method contains large quantities of dissolved chlorine or chlorine-containing compounds. An optical fiber derived from said base material is plagued with an absorption loss in the visible light region (i.e., wavelength band of 0.6-1.1  $\mu\text{m}$ ) due to said dissolved chlorine. Said dissolved chlorine, furthermore, is bubbled during said hollow segment-eliminating process or during a subsequent spinning process.

When the aforementioned internal MCVD method is implemented, a certain amount of heat necessary for inducing the vapor-phase oxidation of the feed gaseous mixture is fed from outside the quartz tube, and the temperature of the quartz glass tube is elevated to the softening point by said external heat. As a result, the quartz tube is easily twisted or sagged. As the thickness of the glass deposition layer increases, the heat transmission efficiency deteriorates, and as a result, it becomes

necessary to increase the external heat level. In such a case, the aforementioned deformations are aggravated. If an oxyhydrogen flame is employed as an external heat source, it is necessary to increase the hydrogen content in order to elevate the heating temperature. In such a case, the flame rate [sic] increases, and as a result, said deformations are significantly aggravated. If said deformations are induced, furthermore, the thickness of the glass deposition layer becomes inevitably heterogeneous, and as a result, the refractive index distribution of the objective quartz glass base material significantly varies, which is extremely inconvenient.

The present invention provides a method for manufacturing a light-transmitting quartz glass base material by the internal MCVD method which is unaccompanied by the aforementioned problems. In other words, the following procedures are carried out: an estersilane represented by the following general formula:



(wherein R<sup>1</sup> is selected from among a hydrogen atom, methyl group, and an ethyl group; R<sup>2</sup> is selected from between a methyl group and an ethyl group; n is a positive number of 0-4) and a dopant represented by one of the following formulae: Ge(OR<sup>3</sup>)<sub>4</sub> or B(OR<sup>3</sup>)<sub>3</sub> (wherein R<sup>3</sup> is a monovalent hydrocarbon group) or PH<sub>3</sub> are heated and combusted in a quartz tube in such a way that the resulting dopant-containing silica will be deposited on the inner wall of said quartz tube as a transparent glass film, and subsequently, said quartz glass tube is heated and melted for the purpose of

eliminating the hollow segment of said quartz tube.

The present invention will be explained in full detail. The present inventors compiled exhaustive research on a method for manufacturing a light-transmitting quartz glass base material which is characterized by a desirable refractive index distribution and which contains no halogen atoms or halogen-containing compounds. After it had been hypothesized that the aforementioned objective would be attained by using a feed silane and a dopant containing no intramolecular halogen atoms as a glass-forming material and a dopant, respectively, additional research was conducted, and as a result, the following were discovered: if an estersilane represented by the aforementioned general formula is employed as said silane, the combustion rate is low since the boiling point is approximately 100°C or higher; moreover, said material is easy to handle and is inexpensive from an industrial point of view; if a germanium, boron, or PH<sub>3</sub> dopant which contains an alkoxy group is employed, a high reactivity can be attained at low /3 temperature, and no halogen atoms are employed [sic: non sequitur]; if the aforementioned feed gas and dopant are utilized, a quartz glass base material which contains no halogen atoms or halogen-containing compounds and which is characterized by an excellent refractive index distribution can be assuredly obtained; if this [sic] is employed, the reactivity difference attributed to the types of gases can be eliminated, and since the reactivity of said gaseous mixture is considerably higher than those employed in conventional methods, the external heat for heating said quartz

tube can be minimized; for example, if an oxyhydrogen flame is employed as said external heat source, the hydrogen concentration can be reduced to 1/5 to 1/2 of those in conventional methods; in such a case, the deformation of the quartz tube is prevented, and as a result, a quartz glass base material characterized by an excellent refractive index distribution is obtained. Upon further research, the present invention has been completed.

As the foregoing explanations clearly demonstrate, the estersilane which is employed as the feed glass-forming material of the method of the present invention is represented by the following general formula:  $R_nSi(OR^2)_{4-n}$ .

Concrete examples of such compounds include methyltrimethoxysilane, dimethyldimethoxysilane, trimethylmethoxysilane, tetramethoxysilane, methyltriethoxysilane, tetraethoxysilane, etc. From an industrial point of view, methyltrimethoxysilane and tetramethoxysilane are especially desirable since they are inexpensive and since they can be easily handled. Said estersilane can be easily synthesized by reacting an alcohol (e.g., methanol, ethanol, etc.) with trimethylchlorosilane or methyltrichlorosilane, which is a byproduct produced in a process whereby dimethyldichlorosilane, which is a main feed material for synthesizing silicone rubbers, silicone varnishes, or silicone oils by directly reacting metallic silicon with methyl chloride, or by reacting an alcohol with a mixture consisting of monomethyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, monomethyldichlorosilane, etc., which is

obtained by pyrolyzing polymethylpolychloropolysilane [or] polymethylpolychloropolysiloxane represented by the following general formula:  $(CH_3)_nSi_mCl_xO_y$ , which is obtained in said dimethyldichlorosilane-manufacturing process [sic: convolution and ambiguity inherent in original]. Said tetramethoxysilane can be manufactured according to the following scheme:



by reacting metallic silicon with methyl alcohol in the presence of an NaOCH<sub>3</sub> catalyst. Said compound is inexpensive and is highly accessible on an industrial basis, and an impurity-free purified product can be easily synthesized by rectifying a corresponding feed chlorosilane or its ester. As a result, a high-purity quartz glass base material can be obtained.

The dopant employed in the present invention is represented by the aforementioned formula Ge(OR<sup>3</sup>)<sub>4</sub>, B(OR<sup>3</sup>)<sub>3</sub>, [or] PH<sub>3</sub>. Concrete examples of applicable compounds include Ge(OCH<sub>3</sub>)<sub>4</sub> (boiling point: 150°C), Ge(OC<sub>3</sub>H<sub>5</sub>)<sub>4</sub> (boiling point: 190°C), Ge(O-n-C<sub>3</sub>H<sub>7</sub>)<sub>4</sub> (boiling point: 240°C), Ge(O-n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub> (boiling point: 290°C), B(OCH<sub>3</sub>)<sub>3</sub> (boiling point: 68°C), B(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (boiling point: 117°C), B(O-n-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub> (boiling point: 176°C), and B(O-n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub> (boiling point: 227°C). In particular, compounds wherein groups corresponding to R<sup>3</sup> are methyl or ethyl groups are especially desirable since the boiling points are relatively low and since they can be easily fed into a reaction container in the presence of a carrier gas. Said Ge(OR<sup>3</sup>)<sub>4</sub> and B(OR<sup>3</sup>)<sub>3</sub> can be manufactured by conventionally-known techniques. For example, said compounds can be effortlessly synthesized according

to the procedures specified in J. Amer. Chem. Soc., 1953, 75, p. 718, J. Chem. Soc., 1956, p. 4916, Encyclopedia of Chemical Technology, Third Edition, Vol. 4, p. 111, etc. The /4 aforementioned PH<sub>3</sub> (boiling point: -88°C) is a representative halogen-free phosphorus-containing compound. This compound is ideal since it induces an extremely high combustion efficiency in the air or oxygen and since it can be easily filled into a cylinder in high purity.

When the method of the present invention is implemented, a mixture consisting of said estersilane, dopant, and gaseous oxygen (i.e., oxidizing agent) (as well as a carrier gas, if necessary) is fed into a quartz tube, and after an oxidizing reaction has been induced within said quartz tube, the resulting dopant-containing silica is deposited on the inner wall of the quartz tube. If the conventional internal MCVD method is implemented, a silica which has been produced from a reactive gas which has been fed into said quartz tube is homogeneously deposited, and accordingly, it is necessary to transport an oxyhydrogen flame burner along said quartz tube in a reciprocal fashion. If the method of the present invention is implemented, on the other hand, both the estersilane and dopant are combustible substances. Immediately after said substances have been combusted at the front end of a feed nozzle which is inserted into the quartz tube, a dopant-containing silica is deposited on the wall of the quartz tube. In the aforementioned process, it is desirable that the quartz tube be transported in a reciprocal fashion while the heat source (e.g., oxyhydrogen flame

burner, etc.) is being fixed. If the rate at which said gaseous mixture is fed into the quartz tube is excessively low, "backfire" may be observed. For this reason, it is desirable that said different mixture be sprayed into the quartz tube at a sufficiently high flow rate. Unless gaseous oxygen is mixed, the combustion rate decreases, and as a result, it becomes difficult to completely combust said gaseous mixture. It is desirable that oxygen be mixed immediately before the feed nozzle.

The silica which has been deposited on the inner wall of the quartz tube is melted by the combustion heat of the feed gaseous mixture or by the heat of an external burner or electrical heater. As a result, a glass film is coated on the inner wall of said quartz tube. Said silica or glass film contains the dopant, and the refractive index depends on the concentration of said dopant. When this method is implemented, therefore, it is desirable that the dopant concentration of the feed gaseous mixture be varied in such a way that a glass film characterized by a certain refractive index distribution will be laminated in the diametrical direction within the quartz tube.

After said dopant-containing layer has been laminated on the inner wall of said quartz tube, said quartz tube is heated and melted in order to eliminate the hollow segment, and as a result, a quartz glass base material is obtained. In such a case, a conventional collapse process can be appropriately utilized. For example, the quartz tube is heated and melted at approximately 2,000°C, and air on the inside is expelled based on the molten

glass viscosity and the glass surface tension.

Next, the method of the present invention will be explained with reference to figures. Figure 1 shows a vertical cross-sectional view of the main components of a device which is utilized for implementing the method of the present invention. Figure 2 shows a vertical cross-sectional view of a process whereby a quartz tube is transported. The feed gaseous dopants which are stored in the estersilane container (1),  $\text{Ge}(\text{OR}^3)_4$  container (2),  $\text{B}(\text{OR}^3)_3$  container (3), and the  $\text{PH}_3$  container (4) are transported by gaseous argon (i.e., carrier gas), which is fed via the tube (5), and after said components have been mixed with gaseous oxygen which has been fed via the conductive tube (7) in the mixer (6), the resulting mixture is fed into the quartz glass tube (8). Said gaseous mixture is sprayed into the quartz tube from the feed nozzle (9). Since the quartz tube (8) is heated by the external oxyhydrogen flame burner (10), said gaseous mixture is combusted at the front end of the feed nozzle (9). In such a case, a dopant-containing silica is produced as a result of oxidation, and said silica is deposited on the inner wall of the rotating quartz tube. Said silica is homogeneously deposited on the inner wall of the quartz tube since said tube engages in a relative movement vis-a-vis the stationary burner. Said silica is melted by the combustion heat of the feed gas and the heat of the burner. As a result, a glass layer is deposited on the inner wall of the quartz tube, and the silica which has not been converted into said glass film and the resulting exhaust gas are removed from the other end of

the quartz tube. Figure 2 pertains to a process whereby said quartz tube is transported. The quartz tube (8) moves from the position shown in Figure a) to the position shown in Figure b) vis-a-vis the fixed burner (10). Immediately after it has been transported to the end (see Figure b)), it is returned to the state shown in Figure a). As a result, a glass film is formed.

In the aforementioned process, the quantity of the dopant with respect to the estersilane is enlarged or lessened over time in such a way that the dopant concentration in the glass film deposited on the inner wall of said quartz tube will satisfy a certain predetermined refractive index distribution, as has been mentioned above. After the thickness of said glass film has reached a certain level, the addition of the feed gaseous mixture is terminated, and the hollow segment of the resulting hollow quartz tube is eliminated by the aforementioned collapse process. As a result, the objective quartz glass base material can be obtained.

When the method of the present invention is implemented, a dopant-containing glass layer is laminated on the inner wall of a quartz tube by the internal MCVD method by using an estersilane containing no halogen atoms or halogen-containing compounds and a dopant as feed materials, and the hollow segment of said tube is eliminated for the purpose of manufacturing a light-transmitting quartz glass base material. As a result, a quartz glass base material which contains absolutely no halogen atoms or halogen-containing compounds (i.e., which is unaccompanied by a light

absorption loss attributed to said halogens) can be obtained. Since the low-temperature reactivity of the aforementioned dopant is excellent, furthermore, the variation of the refractive index distribution can be minimized, and a light-transmitting quartz glass base material characterized by a high specific refractive index difference can be easily obtained. In such a case, furthermore, the temperature of an external heater can be maintained at a low level as compared with the conventional methods, and undesirable deformations of the quartz tube can be prevented. As a result, a quartz glass base material characterized by a desirable refractive index distribution can be effortlessly manufactured.

The following are application examples of the present invention.

#### Application Example 1

An apparatus characterized by the structure shown in Figure 1 was assembled by using a synthetic quartz tube (outer diameter: 20 mm; length: 1,000 mm). After a feed gaseous mixture consisting of methyltrimethoxysilane ( $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ ) and  $\text{Ge}(\text{OC}_2\text{H}_5)_4$  and  $\text{PH}_3$  (i.e., dopants) had been transported by gaseous argon, it was mixed with gaseous oxygen, and the resulting gaseous mixture was fed into said quartz tube from a feeder nozzle.

Said quartz tube was heated by an oxyhydrogen burner. More specifically, said quartz tube was transported at a rate of 150 mm/min. while said burner was being fixed. The compositional ratio of the feed gas, dopants, and oxygen was varied according to Figure

3 while 100 [illegible] cycles were being carried out. As a result, 100 glass film layers characterized by an  $\text{SiO}_2\text{-P}_2\text{O}_5\text{-GeO}_2$  composition was deposited on the inner wall of the quartz tube.

Next, the permeation of the gaseous mixture was terminated, and after the temperature of the external heater had been elevated, the hollow segment of said quartz tube was eliminated, and as a result, a rod-shaped quartz glass base material was obtained.

The resulting quartz glass base material was transparent. When the cross-sectional refractive index distribution was measured, it was determined that said base material was characterized by the graded index type shown in Figure 4. When a fiber derived from said base material was analyzed by using an X-ray microanalyzer, no chlorine atoms were detected. Even when said base material was stretched, no bubbles were produced, and there was absolutely no absorption loss attributed to chlorine atoms.

#### Application Example 2

An apparatus characterized by the structure shown in Figure 1 was assembled by using a synthetic quartz tube (outer diameter: 30 mm; length: 1,000 mm). After a feed gaseous mixture consisting of 100 cc of methyltrimethoxysilane ( $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ ) and 200 cc of  $\text{B}(\text{OCH}_3)_3$  (i.e., dopant) had been transported by using 400 cc of gaseous argon, 1,850 cc of gaseous oxygen was mixed, and after the resulting gaseous mixture had been fed into said quartz tube, treatment procedures identical to those in Application Example 1 were carried out. As a result, 30 layers (i.e., clad layers) consisting of a glass film characterized by an  $\text{SiO}_2\text{-B}_2\text{O}_3$  composition

were laminated on the inner wall of the quartz tube.

Next, 100 cc of methyltrimethoxysilane and 10 cc of PH<sub>3</sub> /6 and 30 cc of Ge(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (i.e., dopants) were transported by using 300 cc of gaseous argon, and after 1,250 cc of gaseous oxygen had subsequently been mixed, the resulting gaseous mixture was fed into said quartz tube, and treatment procedures identical to those in Application Example 1 were carried out. As a result, 70 layers (i.e., core layers) consisting of a glass film characterized by an SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-GeO<sub>2</sub> composition were laminated on the inner wall of the quartz tube.

Next, the permeation of the gaseous mixture was terminated, and after the temperature of the external heater had been elevated, the hollow segment of said quartz tube was eliminated, and as a result, a rod-shaped quartz glass base material was obtained.

When the cross-sectional refractive index distribution of the resulting transparent glass was measured, it was determined that said base material was characterized by the step index type shown in Figure 5a. When a fiber derived from said base material was analyzed by using an X-ray microanalyzer, no chlorine atoms were detected. Even when said base material was stretched, no bubbles were produced, and there was absolutely no absorption loss attributed to chlorine atoms.

#### Application Example 3

An apparatus characterized by the structure shown in Figure 1 was assembled by using a synthetic quartz tube (outer diameter: 30 mm; length: 1,000 mm). After a feed gaseous mixture consisting of

100 cc of tetramethoxysilane ( $\text{Si}(\text{OCH}_3)_4$ ) and 200 cc of  $\text{B}(\text{OC}_2\text{H}_5)_3$  (i.e., dopant) had been transported by using 200 cc of gaseous argon, 2,900 cc of gaseous oxygen was mixed, and after the resulting gaseous mixture had been fed into said quartz tube, treatment procedures identical to those in Application Example 1 were carried out. As a result, 50 layers (i.e., clad layers) consisting of a glass film characterized by an  $\text{SiO}_2\text{-B}_2\text{O}_3$  composition were laminated on the inner wall of the quartz tube.

Next, 100 cc of tetramethoxysilane and 10 cc of  $\text{PH}_3$  and 35 cc of  $\text{Ge}(\text{OCH}_3)_4$  (i.e., dopants) were transported by using 300 cc of gaseous argon, and after 1,000 cc of gaseous oxygen had subsequently been mixed, the resulting gaseous mixture was fed into said quartz tube, and treatment procedures identical to those in Application Example 1 were carried out. As a result, 50 layers (i.e., core layers) consisting of a glass film characterized by an  $\text{SiO}_2\text{-P}_2\text{O}_5\text{-GeO}_2$  composition were laminated on the inner wall of the quartz tube.

Next, the permeation of the gaseous mixture was terminated, and after the temperature of the external heater had been elevated, the hollow segment of said quartz tube was eliminated, and as a result, a rod-shaped quartz glass base material was obtained.

When the cross-sectional refractive index distribution of the resulting transparent glass was measured, it was determined that said base material was characterized by the step index type shown in Figure 5b. When a fiber derived from said base material was analyzed by using an X-ray microanalyzer, no chlorine atoms were

detected. Even when said base material was stretched, no bubbles were produced, and there was absolutely no absorption loss attributed to chlorine atoms.

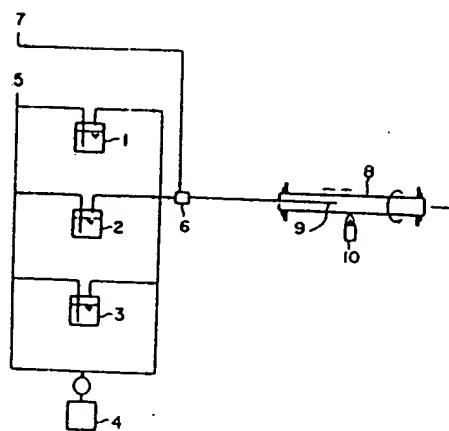
#### 4. Brief explanation of the figures

Figure 1 shows a vertical cross-sectional view of the main components of an apparatus which can be utilized for implementing the method of the present invention. Figure 2 shows a vertical cross-sectional view of a process whereby said quartz tube is transported. Figure 3 is a diagram pertaining to the feed gas, dopant, and gaseous oxygen flow rates in Application Example 1. Figure 4 shows the refractive index distribution of the quartz glass base material obtained in Application Example 1. Figures 5a and b show the refractive index distributions of the quartz glass base materials obtained in Application Examples 2 and 3, respectively.

(1): estersilane container; (2): Ge(OR<sup>3</sup>), container; (3): B(OR<sup>3</sup>)<sub>3</sub>, container; (4): PH<sub>3</sub>, container; (5) and (7): conductive tubes; (6): mixer; (8): quartz glass tube; (9): feed nozzle; (10): burner.

Figure I

1



2

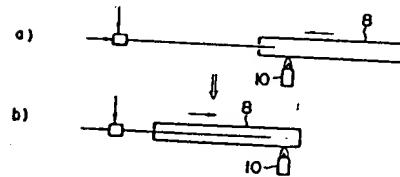
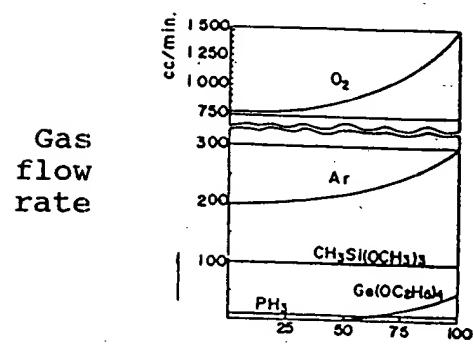


Figure 3

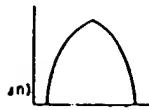
/7



Transporting/heating  
frequency

**Figure 4**

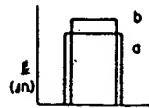
Relative  
radius



Refractive index  
difference

**Figure 5**

Relative  
radius



Refractive index

JN 9090838  
MAY 1985

PRO 91-1045

MTMS - COMBUSTION

w/ Dopant

*✓*  
 $P_2O_5$ *168220*

85-161549/27 SHINETSU CHEM IND KK 25.10.83-JP-198270 (22.05.85) C03b-08/04 C03b-37/* C03c-13/04 G02b-06 Optical quartz glass preform mfr. - by combusting ester silane and dopant inside	L01 V07 P81 SHIE 25.10.83 *J6 0090-838-A	L(1-F)
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C85-070551

Process comprising combusting ester silane of formula R<sub>1</sub>nSi(OR<sub>2</sub>)<sub>4-n</sub> (where R<sub>1</sub> is H or (m)ethyl, R<sub>2</sub> is (m)ethyl, and n is positive number 0-4, pref. methyl trimethoxy silane, tetramethoxy silane etc., and dopant selected from PH<sub>3</sub>, Ge(OR<sub>3</sub>)<sub>4</sub> and B(OR<sub>3</sub>)<sub>4</sub>, where R<sub>3</sub> is mono-valent hydrocarbon radical, e.g. Ge(OCH<sub>3</sub>)<sub>4</sub>, B(OCH<sub>3</sub>)<sub>3</sub> etc., in the inside of a quartz tube to form as laminate a dopant-containing transparent silica glass membrane on the inner wall, and then heating the quartz tube to be fused and collapsed.

**ADVANTAGE** . Preform exhibits low refractive index distribution variation and high specific refractive index difference, and contains no elementary halogen or halogen cpd. (7pp Dwg.No.0/5)

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*TRANSLATION*

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明細書

1. 発明の名称

光伝送用石英ガラス母材の製造方法

特許請求の範囲

1. 一般式  $R_n^3 Si(OR^3)_{4-n}$  [こゝに  $R^3$  は水素原子またはメチル基、エチル基、 $R^2$  はメチル基またはエチル基、nは0~4の正数]で示されるエスチルシランおよび式

$OR^3$ ,  $B(OR^3)_3$

[こゝに  $R^3$  は1価炭化水素基]または  $PH_3$  で示されるドープ剤とを石英管中で加熱焼成させ、これによつて発生するドープ剤を含むシリカを石英管内壁に透明なガラス膜として積層させたのち、この石英管を加熱溶融して中実化することを特徴とする光伝送用石英ガラス母材の製造方法。

3. 発明の詳細な説明

本発明は光伝送用石英ガラス母材の製造方法。特には内付けMCVD法により元素状または化合物状の塗布を含有しない光伝送用石英ガラス母材を製造する方法に関するものである。

光伝送用石英ガラス母材の製造方法については各種の方法が知られているが、これにはそれが純度の極めて高いものとする必要があり、さらには断面方向の屈折率制御を行なう必要があるということから化学反応を利用した化学気相沈着法(CVD法)が汎用されている。そして、このCVD法については、けい素化合物の液化により得られるシリカを石英管内に透明なガラス膜として形成させる内付け法(MCVD法)、芯材の外表面にけい素化合物の火炎加水分解で作ったシリカを堆積させる外付け法、さらには回転しつつある耐火性物質にけい素化合物の火炎加水分解で作ったシリカを塗り



ができる。また、このPH<sub>3</sub>（沸点-88℃）については、リンの化合物の中でもこれがハロゲンを含まない代表的な化合物であり、空気中あるいは酸素中においてもきわめて高い燃焼効率を示すこと、ポンベに充填した形態で高純度のものが簡便に得られることなどの理由で最適とされる。

本発明の方法はこのエステルシランとドープ剤との混合ガスとを必要に応じキャリヤーガスで搬送し、酸化剤としての酸素ガスと共に石英管内に送入し、この石英管内で酸化反応を行なわせ、これによつて発生したドープ剤を含むシリカを石英管の内壁に堆積させることによつて行なわれる。なお、従来公知の内付けMCVD法ではこの石英管内に送入された反応ガスから発生するシリカを石英管内壁に均一に堆積させるために、この石英管内に沿つて酸素炎バーナーを順次移動させ、これを往復運動させる必要があつたけれども、本発明の方法ではこのエステルシラン、ドープ剤が

つて異なる屈折率を示すので、この実施に当つては石英管内の内径方向に順次所定の屈折率をもつガラス膜が順次に堆積されるように原料混合ガス中のドープ剤濃度を順次変えるようにすることがよい。

また、このようにして得られたドープ剤を含むガラス膜をその内壁に堆積した石英管はついでこれを加熱溶融して中実化し、石英ガラス母材とするのであるが、これは従来公知のコラプス工程を適用すればよく、これには例えばこの石英管を2,000℃程度で加熱溶解させ、溶融したガラスの粘性、ガラスの表面強力をを利用して内側に空気が残らないようにしてこれを中実につぶすという方法を探ればよい。

つぎに本発明方法を添付の図面にもとづいて説明する。第1図は本発明方法を実施するための装置の断面図、第2図はその石英管の移動を示す概略面図を示したものであり、エステルシラン

#### 特開昭60-90838(4)

いずれも可燃性物質であり、これらは石英管への送入のためのフィードノズル先端で燃焼して直ちにドープ剤を含むシリカとなり石英管壁に堆積されるので、この実施に当つては酸素炎バーナーなどの加熱源を固定しておいて石英管自身を移動させ、往復運動させるほうが好ましい。また、これらの原料ガスの石英管への送入はその速度が小さいと逆火現象を伴なうおそれがあるので、これは十分な流速で石英管内に噴射することがよく、またこれに酸素ガスを混入しないとその燃焼速度が低下し完全燃焼が達成されなくなるおそれがあるので、これにはフィードノズルの直前で酸素を混入することが好ましい。

なお、この石英管内に堆積されたシリカは原料ガスの燃焼熱および外部からのバーナーあるいは電気加熱によって溶融して石英管の内壁にガラス膜として被着されるが、このシリカないしガラス膜はドープ剤を含んでおり、このドープ剤量によ

(a) 第1図  
石英管の他端から外部に  
の石英管の移動を示した  
定されているバーナー  
a) 図から b) 図のよう  
に末端まで移動した後は  
帰するという手段で順次  
ことが示されている。  
この場合、前記したよ  
するドープ剤の添加量は  
ガラス膜中に含まれるト  
られた屈折率を示すよう  
加または減少するよう  
が所定の厚さになつたと  
め、ついでこゝに角から  
たコラプス工程で処理し  
する石英ガラス母材を  
これを製するに、本  
ハロゲン化合物を含有

シ容積1.00(OR<sup>3</sup>)、容積2. B(OR<sup>3</sup>)、容器3. PH<sub>3</sub>、容器4に収容された原料ガスドープ剤はそれぞれ管5から導入されるキャリヤーガスとしてのアルゴンガスに搬送され、これらは混合器6で管7から送られる酸素ガスと合して石英ガラス管8に送入される。これらのガス送入はフィードノズル9から石英管内に噴射されるが、この石英管8がその外部から酸素炎バーナー10で加熱されているため、こゝに送入されたガスはフィードノズル9の先端で燃焼し、この酸化反応によつてドープ剤を含むシリカとなり、このシリカは回転している石英管内壁に堆積される。このシリカの堆積は静止しているバーナーに対し石英管がその端部から他端にまで順次移動されるので、この石英管の内壁に均一に堆積され、このシリカは原料ガスの燃焼熱およびバーナーからの加熱で溶融し、ガラス膜として石英管壁に堆積され、このガラス膜化されなかつたシリカおよび排ガスは

外径30mm、長さ1用ひて、第1図に示し  
ガスとしてメチルトリ  
(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>、ドープ  
およびPH<sub>3</sub>を使用し  
搬送し、酸素ガスと混  
ら石英管内に供給する  
そして、この石英管  
することとし、このノ  
15.0m／分の速度  
の移動加熱を100回  
ブ剤、酸素の量を第  
て、石英管の内壁に  
成をもつガラス膜を  
ついで、この原料  
熱の温度をあげてこ  
状の石英ガラス母材  
この石英ガラス母材

特開昭60-90838(2)

ついでこのガラス模倣を実化して石英ガラス母材ため、この方法で得られることは塩基化合物が多く、存積によってこれからについてはその可視領域での吸収損失が生じると、の消存率は上記した中、の吸収率において免拂るものである。

V.D法では上記したよう、が生じるに必要な熱が、この外側からの加熱、文化直にまで加熱される、これやだわみが発生し易く、模倣が厚くなるにした、それに応じて外側からなるので、この変形が

中で加熱燃焼させ、こ、剤を含むシリカを石英にて模倣させたのち、こ、実化することを特徴と

月者らは特にハロゲンを含めず、好ましい石英ガラス母材の製について、ガラス形成の分子中にハロゲンおよびドープ剤を使用して研究を行ない、一般式で示されるエス、が沸点が概ね1000℃取扱いも容易で、しと、またこのドープ剤を含むゲルマニすればそれらがハロ

(ねじ式) (2)

ゲン原子を含ます。低温での反応活性も高いものであることから、これらの原料ガス、ドープ剤を使用すれば確実にハロゲン原子またはハロゲン化合物を含まない。しかも良好な屈折率分布をもつて得られる。しかし、この方法で得られるのは、石英ガラス母材が得られるほか、これによればこれらガスの種類による反応活性の違いがなくななる小孔が形成される。これは、このガスが熱を帯び、さすにはこれらのガスが従来法のものにくらべて高反応性であることからこの石英管を外部から加熱するための熱量が少なくてすみ、例えばこの加熱炉内に、このガスを吹き込むことで、このガスの外部加熱部を液体窒素とする場合には、この加熱のための水蒸気量を従来の1/5~1/2とすることができる。これが可能となるので、火炎を弱くすることができ、結果において石英管の変形が防止されるので目的とする石英ガラス母材の屈折率分布が良好になると、いうことを見出し、これらの諸条件についてさらに検討を重ね、本発明を完成させた。

本発明の方法においてガラス形成原料とされるエスチルシランは前記したように一般式

特開昭60-90838(3)

$R_n^1Si(OR^2)_4-n$  で示されるものであり、これにはメチルトリメトキシシラン、ジメチルトリメトキシシラン、トリメチルメトキシシラン、テトラメトキシシラン、メチルトリエトキシシラン、テトラエトキシシランなどが例示されるが、これは安価であり扱いやすいということから工業的にはメチルトリメトキシシラン、テトラメトキシシランとすることがよい。このエスチルシランはメチルクロライドと金属性イオンとの酸化反応による、シリコーンゴム、シリコーンワニス、シリコーン油の主原料とされるジメチルジクロロシラン合成時の副生物であるトリメチルクロロシラン、メチルトリグロロシランをメタノール、エタノールなどのアルコールと反応させるか、あるいはこのジメチルジクロロシランの製造工程で得られる一般式  $(OH_3)_nSi_mO_xCl_y$  で示されるポリメチルポリクロロポリシラン、ポリメチルポリクロロ

ポリシロキサンを熱分解して得られるモノメチルトリクロロシラン、ジメチルジクロロシラン、トリメチルクロロシラン、モノメチルジクロロシランなどの混合物をアルコールと反応させることによつて容易に得ることができる。このテトラメトキシシランは金属イオンとメチルアルコールを触媒としての  $NaOCH_3$  の存在下に反応させて、次式

$$Si + 4OH_3 \xrightarrow{NaOCH_3} Si(OH_3)_4 + 2H_2$$

によって製造することができる。これは工業的に安価に供給することができる。これはまたその原料であるジクロロシランまたはそのエスチルシランの精留によつて容易に不純物を含まない精製物として取得することができる。これによれば純度の高い石英ガラス母材が得られるという有利性が与えられる。

他方、本発明の方法で使用されるドープ剤は前

記した式  $Ge(OR^3)_4$  、  $B(OR^3)_3$  、  $PH_3$  で示されるものであり、これには  $Ge(OCH_3)_4$  (沸点150°C)、  $Ge(OCH_3)_3$  (沸点190°C)、  $Ge(O-n-C_3H_7)_4$  (沸点240°C)、  $Ge(O-n-C_4H_9)_4$  (沸点290°C)、  $B(OCH_3)_3$  (沸点68°C)、  $B(OCH_3)_2$  (沸点117°C)、  $B(O-n-C_3H_7)_3$  (沸点176°C)、  $B(O-n-C_4H_9)_3$  (沸点227°C) などが例示されるが、これらのなかでは  $R^3$  基がメチル基、エチル基であるものが比較的沸点が低く、キャリヤーガスへの同伴で反応器内に供給することができる。これが好ましいものとされる。なお、この  $Ge(OR^3)_4$  、  $B(OR^3)_3$  の製造法は公知であり、これは例えば J.Amer.Chem.Soc., 1953, 75, p. 718, J.Chem.Soc., 1956, p. 4916, Encyclopedia of Chemical Technology 第3版、4巻、p. 111などに記載されている方法で容易に得るこ

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であり、これらは石英管へのドノズル先端で燃焼して直ちにシリカとなり石英管壁に堆積させ当つては酸素炎バーナーにおいて石英管自身を移動するほうが好ましい。また、これを管への送入はその速度が小ようおそれがあるので、これまに噴射することがよく、と混入しないとその燃焼速度は成されなくなるおそれがある「ードノズルの直前で酸素をい。

うに堆積されたシリカは原料ト部からのバーナーあるいはして石英管の内壁にガラス化、このシリカないしガラス化おり、このドープ剂量によ

る。

石英管の他端から外部に挿出される。第2図はこの石英管の移動を示したものであり、これには固定されているバーナー10に対し、石英管8がa)図からb)図のように移動され、b)図のように末端まで移動した後は直ちにa)図の状態に復帰するという手段で順次ガラス膜を形成していることが示されている。

実施例

この場合、前記したようにエステルシランに対するドープ剤の添加量はこの石英管に堆積されるガラス膜中に含まれるドープ剤濃度が予め定められた屈折率を示すように、時間の経過と共に増加または減少するように調整され、このガラス膜が所定の厚さになつたときに原料ガスの供給を止め、ついでこれに得られた中空の石英管を前記したコラプス工程で処理して中実化すれば、目的とする石英ガラス母材を得ることができる。

これを要するに、本発明の方法はハロゲン原子、ハロゲン化合物を含有しないエステルシランおよ

特開昭60- 90838(5)

びドープ剤を始発材として内付けMCVD法で石英管内壁にドープ剤を含むガラス膜を複層させ、この浴融中実化によって光伝送用石英ガラス母材を製造するものであり、これによればハロゲン原子、ハロゲン化合物を全く含まない、したがつてハロゲン分の存在による光吸収損失のない石英ガラス母材を容易に得ることができ、これはまたこのドープ剤が低温での反応率のよいものであることから屈折率分布の変化が小さく、比屈折率差の大きい光伝送用石英ガラス母材が容易に得られ、この場合には外部からの加熱を従来法にくらべて低温とすることができますので石英管の変形を防止することができ、結果において好ましい屈折率分布をもつ石英ガラス母材の取得が容易になるといき有利性が与えられる。

つぎに本発明の実施例をあげる。

実施例 1

外径30mm、長さ1000mmの合成石英管を使用して、第1図に示したような装置を作り、原料ガスとしてメチルトリメトキシシラン( $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ )、ドープ剤として $\text{Ge}(\text{OC}_2\text{H}_5)_4$ および $\text{B}_2\text{O}_3$ を使用し、これらをアルゴンガスで搬送し、酸素ガスと混合してフィーダーノズルから石英管内に供給するようにした。

そして、この石英管は酸素炎バーナーで加熱することとし、このバーナーを固定して石英管を150mm/分の速度で移動させることとして、この移動距離を100回行なう間に原料ガス、ドープ剤、希釈ガスを第3図に示したように変化させて、石英管の内壁に $\text{SiO}_2-\text{B}_2\text{O}_3-\text{GeO}_2$ の組成をもつガラス膜を100層形成させた。

ついで、この原料ガスの供給を停止し、外部加熱の温度をあげてこの石英管を中実化してロッド状の石英ガラス母材とした。

この石英ガラス母材は透明であり、この断面に

ついての屈折率分布を測定したところ、これは第4図に示したようなグレーディエント・インデックス型であり、これから作ったファイバーについてX線マイクロアナライザーで分析したところ塩素原子は検出されず、また、この母材は延伸しても充泡は起らず、塩素原子に起因する吸収損失も全くなかつた。

実施例 2

外径30mm、長さ1000mmの合成石英管を使用して第1図に示したような装置を作り、原料ガスとしてのメチルトリメトキシシラン100cc(毎分値、以下同じ)、ドープ剤としての $\text{B}(\text{OC}_2\text{H}_5)_3$  200cc、をアーピングガス400ccで搬送し、これに酸素ガス1,850ccを混合して石英管に送入し、実施例1と同様に処理して $\text{SiO}_2-\text{B}_2\text{O}_3$ の組成をもつガラス膜を石英管内壁にグラウド膜として30層形成させた。

特開昭60-90838(6)

つぎに、この原料ガスとしてのメチルトリメトキシラン1000.c.c., ドープ剤としてのPH<sub>3</sub>100.c.c. とGe(OCH<sub>3</sub>)<sub>4</sub>300.c.c. とをアルゴンガス3000.c.c. で搬送し、これに塩素ガスを12500.c.c. 混合してから石英管に送入し、実施例1と同様に処理してSiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-GeO<sub>2</sub>の組成をもつガラス膜をコア層として70層形成させた。

その後、原料ガスの供給を停止し、外部加熱源の温度をあげてこの石英管を中実化してロッド状の石英ガラス母材とした。

得られた透明なガラス体についてその断面の屈折率分布を測定したところ、これは第5図aに示したようなステップインデックス型であり、これから作ったファイバーをX線マイクロアナライザーで分析したところ、これには塩素原子が全く検出されず、またこの母材は延伸しても気泡が起らず、塩素原子の存在に起因する吸収損失も全くな

かつた。

#### 実施例3

外径30mm、長さ1000mmの合成石英管を使用して第1図に示した装置を作り、原料ガスとしてのテトラメトキシラン[Si(OCH<sub>3</sub>)<sub>4</sub>]1000.c.c. ドープ剤としてのB(OCH<sub>3</sub>)<sub>3</sub>2000.c.c. をアルゴンガス2000.c.c. で搬送し、これに塩素ガス29000.c.c. を混合して石英管に送入し、実施例1と同様に処理してSiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>の組成をもつガラス膜をクラッド層として50層形成させた。

つぎに、この原料ガスとしてのテトラメトキシラン1000.c.c. とドープ剤としてのPH<sub>3</sub>100.c.c. Ge(OCH<sub>3</sub>)<sub>4</sub>350.c.c. とをアルゴンガス3000.c.c. で搬送し、これに塩素ガス1000.c.c. を混合して石英管に送入し、実施例1と同様に処理してSiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-GeO<sub>2</sub>の組成をもつガラス膜をクラッド層として50層形成させた。

つガラス膜をコアとして50層形成させた。

その後、原料ガスの供給を停止し、外部加熱源の温度を上げてこの石英管を中実化してロッド状の石英ガラス母材とした。

得られた透明なガラス体についてその屈折率分布を測定したところ、これは第5図bに示したようなステップインデックス型であり、これから作ったファイバーをX線マイクロアナライザーで分析したところ、これには塩素原子が全く検出されず、またこの母材は延伸しても気泡せず、塩素原子の存在に起因する吸収損失も全くなかつた。

#### 4. 図面の簡単な説明

第1図は本発明方法を実施するための装置の概断面図、第2図はその石英管の移動を示す概断面図、第3図は実施例1における原料ガス、ドープ剤、酸素ガスのガス流量を示すグラフ、第4図は実施例1、第5図a、bはそれぞれ実施例2、

3で作られた石英ガラス母材の屈折率分布図を示したものである。

- 1…エスカルシラン容器。
- 2…Ge(OR)<sub>4</sub>容器。
- 3…B(OR)<sub>3</sub>容器。
- 4…PH<sub>3</sub>容器。
- 5、7…導管、6…混合器。
- 8…石英ガラス管。
- 9…フィードノズル。
- 10…バーナー。

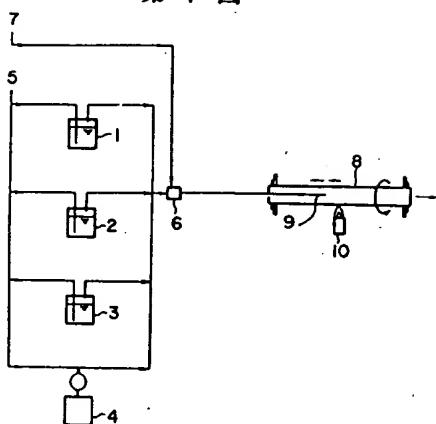
特許出願人 信越化学工業株式会社

代理人 弁理士 山本亮

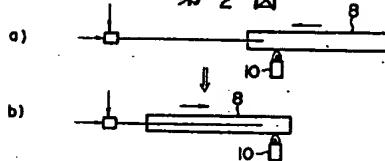


図面の添付(内容に変更なし)

第1図

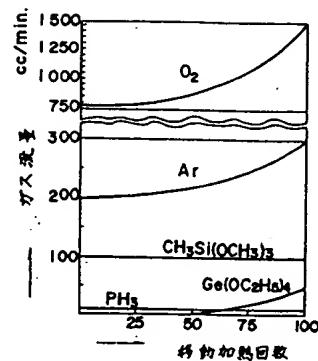


第2図

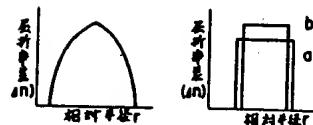


第1図

第3図



第4図 第5図

手続補正書  
昭和59年 2月10日

特許庁長官 若杉和夫殿

通

## 1. 事件の表示

昭和58年特許願第198270号

## 2. 発明の名称

光伝送用石英ガラス母材の製造方法

## 3. 補正をする者

事件との関係 特許出願人

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## 4. 代理人

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## 5. 補正命令の日付

発送日 昭和59年 1月31日

## 6. 補正の対象

図面

## 7. 補正の内容

別紙の通り

